JPW

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

BOWLES, P. et al. Atty. Ref.: 124-1071; Confirmation No. 2793

Appl. No. 10/786,418 TC/A.U. 1745

Filed: February 26, 2004 Examiner:

For: IMPROVED ELECTRODE ASSEMBLY

* * * * * * * * * * * *

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

JOINT DECLARATION UNDER 37 C.F.R. §1.132 AND MPEP §715.01(C)

We, Peter George BOWLES, Emmanuel Imasuen EWEKA, Cyril Olakunle GIWA and Andrew Grahame RITCHIE hereby declare we are joint inventors of the above-identified patent application as evidenced by our joint inventors declaration of record in said application. That we are British subjects residing in the United Kingdom as stated in our declaration and that at the time the invention described in the subject application was made we were employed by QinetiQ Limited, the assignee and owner of the subject application.

That, together with Alex GILMOUR, we are authors of a paper entitled Development of 25 Ah and 50 Ah Lithium / Polycarbon Monofluoride Envelope Cells, copy attached, as presented on March 20, 2003 to The 20th International Seminar & Exhibit on Primary & Secondary Batteries in Fort Lauderdale Florida, USA. Gilmour was an employee of Lexcel Technology Ltd. in the spring of 2003 and Lexcel furnished materials to QinetiQ Limited under contract.

That the pouch batteries and methods of making same described and claimed in the subject application are the joint invention of the four of us, that is Messrs Bowles, Eweka, Giwa and Ritchie, all employees of QinetiQ Limited at the date of invention, and while we acknowledge Gilmour produced coatings of materials for the Lithium/Polycarbon Monofluoride

cells used, in accordance with our instructions, in the underlying research project as reported in the March 20, 2003 presentation. Gilmour did not make any inventive contribution to the subject matter claimed in the above-identified application and we do not regard Gilmour as an inventor of the subject matter of the above-identified application.

We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Peter George BOWLES _____ date: 14/1/05

Emmanuel Imasuen EWEKA _____ date: 14/01/2005

Cyril Olakunle GIWA _____ date: 14/01/2005

Andrew Grahame RITCHIE _____ date: 15/1/2005

Development of 25 Ah and 50Ah Lithium / Polycarbon Monofluoride Envelope Cells

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1. ABSTRACT

QinetiQ, formerly part of the British Government's Ministry of Defence Evaluation and Research Agency (DERA), has developed lithium / polycarbon monofluoride primary cells in the envelope format. These cells have shown high energy density, approaching 700 Wh/kg. Further development has been carried out to study new electrolytes for low temperature performance.

Additionally, there is a requirement for 50 Ah lithium / polycarbon monofluoride (Li/CF_x) primary envelope cells to provide a new operational option for military equipment. This programme aims to ultimately develop a high voltage multi-string Li/CF_x battery based on 50 Ah modules. In previous work we presented results from 1.12 to 18Ah envelope cells. Recently we have scaled up to 25 Ah, 36Ah and 50 Ah cells. During the discharge of 36 Ah cells, an average capacity of 32Ah was realised at 0.05mA/cm^2 to an end point of 2.0 volts. This result is equivalent to an energy density of 480 Wh/kg and corresponds to 88.9% cell efficiency. The development and performance of multi-string 25 Ah cells for military applications will be discussed.

2. INTRODUCTION

Previous work [1,2] has shown that the lithium / polycarbon monofluoride (Li/CF_x) system gives very high energy densities (650 Wk/kg) when lightweight plastic packaging is used. Further development is reported on testing of electrolytes in the cells over a wide range of temperatures and current densities. A new electrolyte salt, lithium bis - oxalato borate, $LiB(C_2O_4)_2$, for lithium batteries has recently been announced [3,4] and this has been tested in these primary batteries as it is potentially cheaper and safer than the existing fluorinated electrolyte salts. We have carried out further development of the scale - up and of the design, with particular emphasis on safety. In order to improve safety in large cells, a safety separator Celgard 2430 was used. For assembly of cells into a battery pack, electronic controls will be used as current limiters to avoid over currents, e. g. short circuits, or over - discharge of cells. In this work, we have considered the use of a 25Ah or a 50 Ah cell module as the building block for a 15 volt 300 Ah battery. For the initial battery pack, 25Ah envelope cells were used, because a large quantity of this size was available.

[1] Presenter of paper

3. CELL FABRICATION AND DISCHARGE REGIME

Laboratory and envelope cells have been described previously [2]. Lithium metal foil backed on to copper mesh was obtained from Chemetall and the polycarbon monofluoride was obtained from Lodestar. The electrolytes used were lithium tetrafluoroborate in propylene carbonate (PC) / di-methoxy ethane (DME) and $LiB(C_2O_4)_2$, also in DME. The dimensions of the positive electrodes were (2080 mm x 90 mm). The coating contained 85% of active cathode composite by weight. The separator was a tri-layer laminate of polypropylene - polyethylene - polypropylene that acts as a shut - down separator, should the cell overheat. In addition, the lithium foil was pressed on to a copper mesh so that electrical contact can be made throughout the anode, even if the lithium foil becomes fragmented as the cell is discharged. The contact resistance of the anode terminal of cells was reduced by the used of a solvent technique to remove unwanted lithium metal from the anode. As a result the contact resistance was significantly reduced. Cells were assembled by folding three layers of anode, separator and cathode by a continuous zigzag folding procedure. The folding machine developed for the folding technology is shown in figure 1a and the cells in figure1b.

Nominal capacity tests were carried out at the following rates: 10, 40, and 100 hour rates. These rates were applied because medium and low rates are of interest. Further discharge tests were carried out at lower temperatures (0, -10, -20 and –40°C).

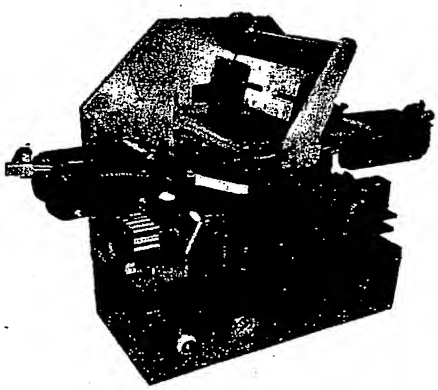


FIG 1a FOLDING MACHINE

FIG 1b 25, 30 and 50Ah ENVELOPE CELLS

4. DISCUSSION OF RESULTS

DISCHARGE OF 25 AND 30 Ah CELLS

Cells have previously been reported at capacity up to 18Ah [1]. Typical discharge curves obtained for 25 and 30Ah envelope cells are presented in figures 2 and 3 respectively. For a 25Ah cell a capacity of 24.3Ah was achieved. In the case of the 30Ah cell the capacity obtained was in excess of 29Ah and the utilisation in terms of duration was 96%. For this cell the specific energy was five hundred watts hour per kilogram.

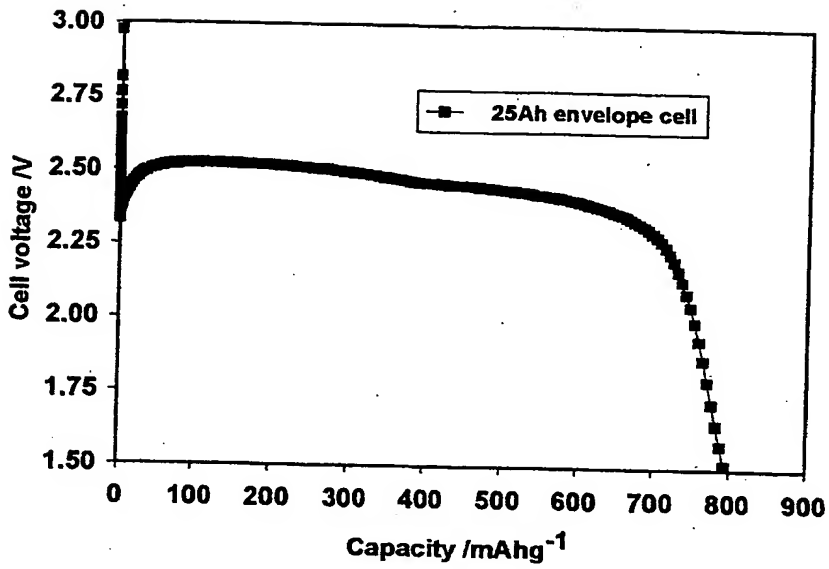


Figure 2. Discharge of 25 Ah cell.

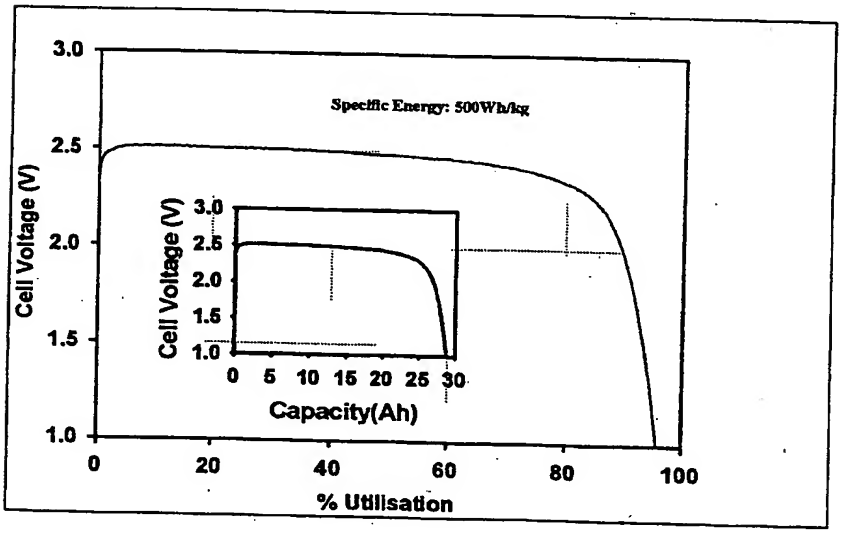


Figure 3. Discharge of 30 Ah cell.

DISCHARGE OF 36 AND 50 Ah CELLS

Cells have now been scaled up to 36 and 50Ah. The discharge of a 36Ah cell is shown in figure 4; a capacity of 32 Ah was obtained at a current loading of 0.05mA/cm^2 to a current cut-off at 2.0 volts. This result indicates that the energy density obtained was 480Wh/kg, which corresponds to 88.9% cell efficiency. Figure 5 shows the discharge result for the 50Ah cell. The specific energy density for the 50Ah cell was 510Wh/kg and this results appears to be slightly higher than that for the smaller size cells. Furthermore, cell utilisation of 98% for the largest size cell is also higher than previously reported. These cells are suitable for applications

that require low to medium current loads such as electronics communications equipment and cells can also sustain a few amps for limited period of time. A summary of the discharge results obtained for various size of envelope cells is shown in table 1.

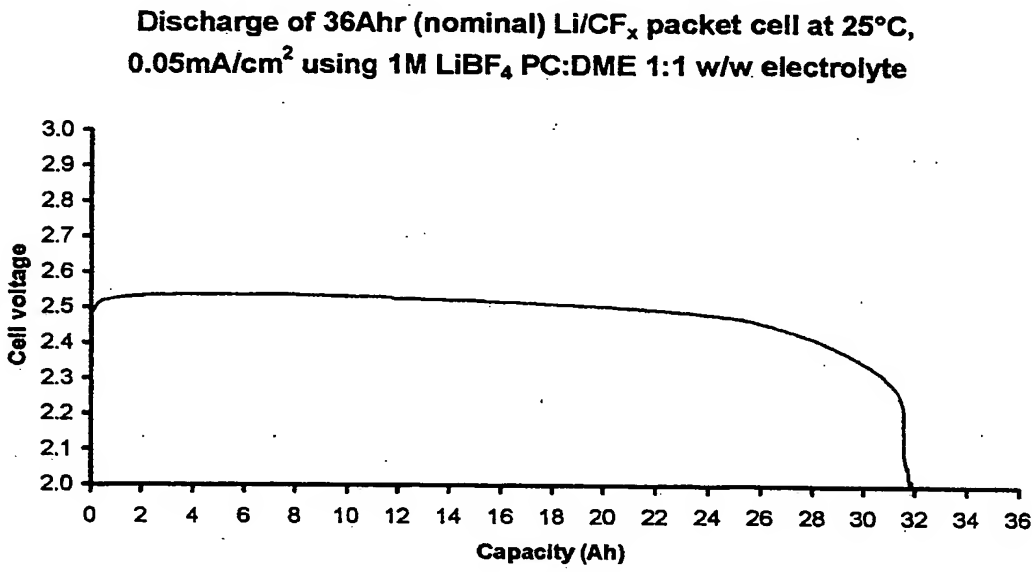


Figure 4. Discharge of 36 Ah cell

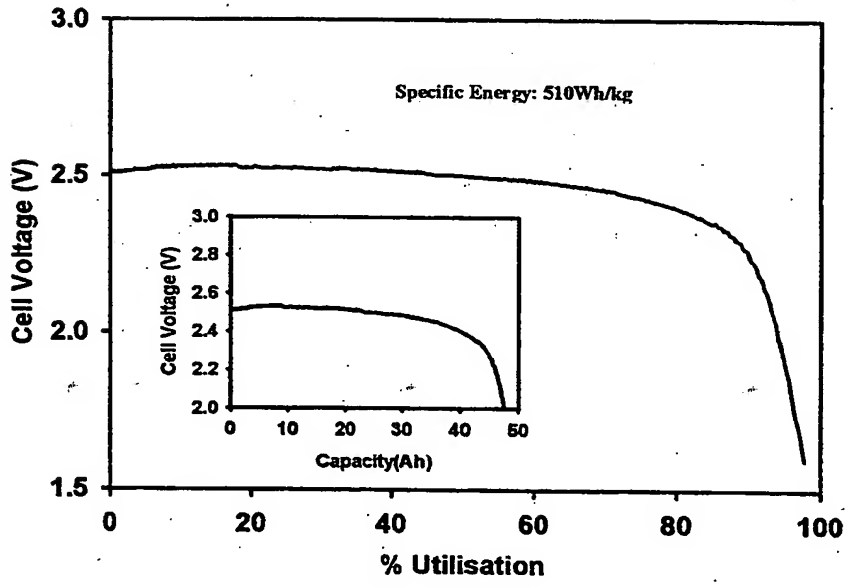


Figure 5. Discharge of 50 Ah cell.

PERFORMANCE OF A SERIAL SIX-STRING 15 VOLTS BATTERY

Figure 6 illustrates the result for the discharge of a 6 x 25Ah series string for a Li/CF_x battery pack. All cells in the string were discharged at C/100 rate to a 1 volt cut-off. The utilisation of the string to a cut-off voltage of 10.5 volt was above 90% and the specific energy density was 496 Wh/kg (740 Wh/l). The discharge profiles for the single cells in the series string are shown in the inset (figure 6) and all six cells were at least 90% utilised to a cut-off voltage of 1 volt. This result indicates that a battery pack based on lithium / polycarbon monofluoride could power electronic devices; furthermore the current capability can be increased by the introduction of parallel strings. We intend to test series - parallel string combination during the next phase of this programme.

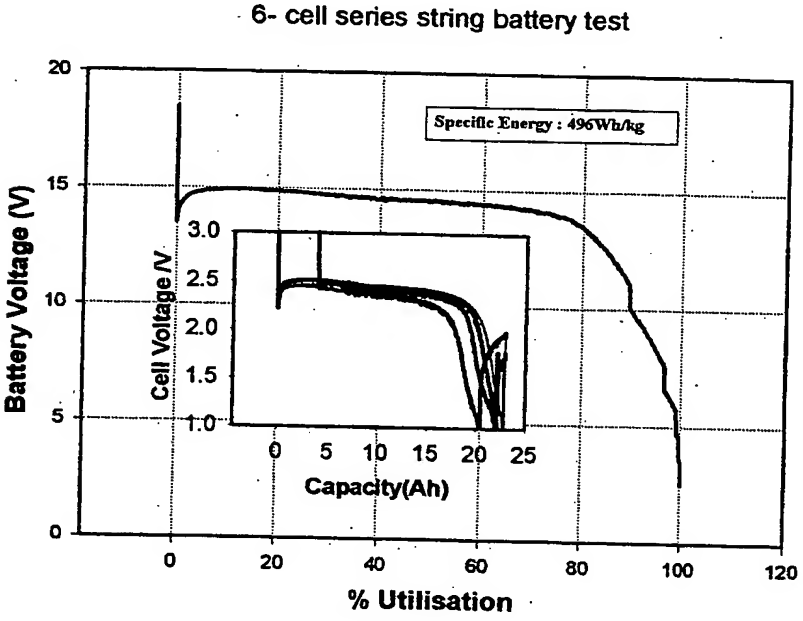


Figure 6. Discharge of series string of 6 x 25 Ah cells.

LITHIUM BIS - OXALATO BORATE ELECTROLYTE SALT

One area of interest is safer and cheaper electrolyte salts to replace fluorinated salts. Lithium bis - oxalato borate, ($LiB(C_2O_4)_2$) has been proposed as new salt for lithium - ion batteries [3,4]. It has been tested here for lithium primary batteries. Discharges over a range of currents at room temperature are shown below in figure 7.

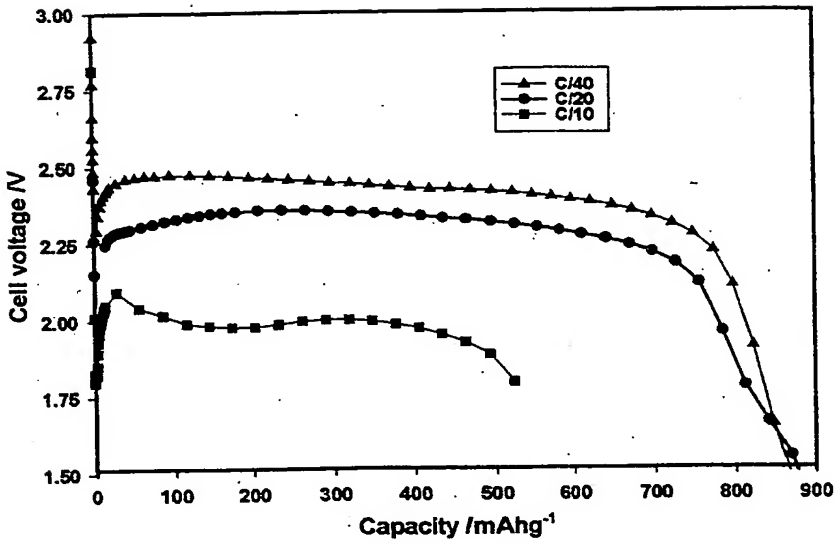


Figure 7. Discharges using lithium bis - oxalato borate electrolyte.

This figure shows good discharges at the 20 and 40 hour rates. Cells using this electrolyte have been tested over a range of temperatures (see figure 8). Reasonable discharges were found at 0 and 20°C but poor result at –10°C. The cause for the poor performance at low temperatures can be seen from the early stages of the discharge. This shows that the voltage drops on applying load, i. e. the internal resistance increased rapidly as the temperatures were reduced. Hence this new electrolyte is satisfactory at moderate rates (20 hour or slower) and at moderate temperatures (0°C and above).

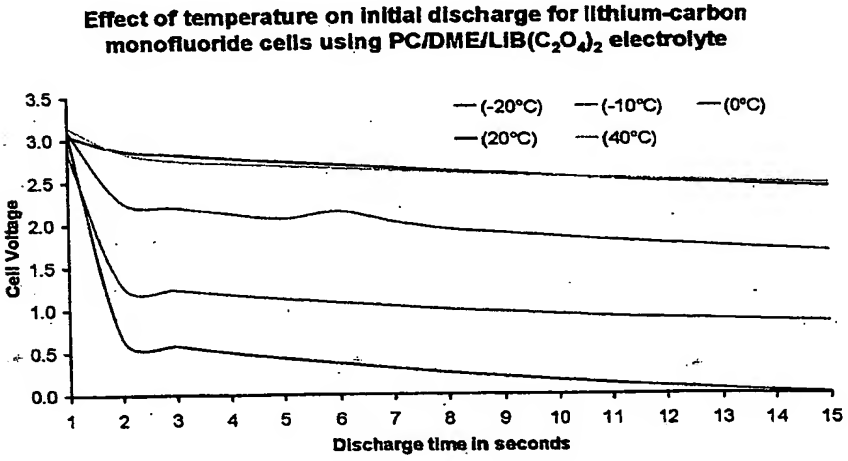


Figure 8. Discharges of cells at -20 to +40°C.

SAFETY CONSIDERATIONS

For making large size lithium / polycarbon monofluoride envelope cells, it is essential to ensure the safety of the product. A safety separator (Celgard 2430) has been selected and a new form of lithium foil has been used in which the lithium is pressed into a copper mesh to prevent fragmentation of the lithium. It is necessary to determine the performance of these materials. A test at room temperature and at the 40 hour rate was chosen to compare standard and safety materials. It can be seen that the discharges are very similar for the standard lithium foil and the existing separator (Celgard 3501) and for lithium foil backed on copper mesh and with safety separator (Celgard 2430). There is therefore no performance limitation to using the safety materials (see figure 7). However, further storage tests and safety tests are to be carried out when sufficient cells have been produced.

EFFECT OF STORAGE ON CELLS PERFORMANCE

A preliminary study of 25Ah cells over a short period was done to obtain an indication that room temperature storage might be possible without serious degradation in performance. Cells were stored over 42 days at room temperature and then discharged. Results obtained showed that cell did not degraded under this condition

5. FURTHER WORK

The cells developed here could be used to develop other large size batteries, e.g. the lithium primary BA5590 battery. Potential benefits are described in table 2 (below). Further electrolyte development could improve electrolyte performance.

6. CONCLUSIONS

Assembly of lithium / polycarbon monofluoride envelope cells has been progressed up to 50Ah stage, with satisfactory performance. The light weight plastic packaging reduces the weight of batteries relative to those using metal cans.

Lithium bis - oxalato borate has been tested as a possible electrolyte salt for lithium primary batteries. Satisfactory performance was found at moderate rates (20 hour and slower) and at moderate temperatures (0°C and above).

New materials, lithium backed on to copper foil and tri-layer separator, have been selected for large size envelope cells to improve safety.

We have successfully tested a 15 volt; 6-series string battery and cell utilisation was very good.

7. REFERENCES

1. C. O. Giwa, A. G. Ritchie, P. G. Bowles, E. L. Price, J. Burgess, A. Gilmour, and J. Allan, Scale-up of Lithium Carbon Monofluoride Envelope Cells, pp 32-35, Proceeding of the 39th Power Sources Conference, Cherry Hill, NJ, USA, June 2000.

2. A. G. Ritchie, C. O. Giwa, P. G. Bowles, J Burgess, E. I. Eweka, and A. Gilmour, Further Development of Lithium / Polycarbon Monofluoride Envelope Cells, pp 180-183, Power Sources 18, Proceedings of the 22nd International Power Sources Symposium, Manchester, May 2002, Journal of Power Sources, 96 (2001).

3. U. Wietelmann, Lithium Bisoxalatoborate, The Production of and its Use as a Conducting Salt, European Patent EP 1091963, 18th April 2001, PCT WO 00/00495, 6th January 2000.

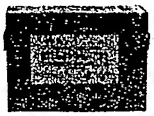
4. U. Wietelmann, Lithium Bis (Oxalato) Borate (LOB): A New Conducting Salt with Excellent Stability Properties, Batteries 2001, Paris, April 2001.

TABLE 1. SUMMARY OF CELL PERFORMANCE

Nominal Capacity (Ah)	Achieved Capacity (Ah)	Specific Energy (Wh/kg)	Energy Density (Wh/l)
25	24.3	500	744
30	29.4	500	740
36	32.0	480	720
50	48.0	510	740

TABLE 2. POSSIBLE BA5590 LITHIUM / POLYCARBON MONOFLUORIDE BATTERY

Comparison of typical military batteries

Chemistry	BA5590/ U  Li/ SO_2	Li/ CF_x (design projection)	Primary Clansman  Li/ SO_2	Li/ CF_x (design projection)
Nominal voltage	14/ 28V	12.5/ 25V	28V	25V
Nominal capacity	7.5/ 15Ah	20/ 40Ah	16Ah	34.4Ah
Weight	1.02kg	1.17kg	2.19kg	2.16kg
Volume	0.88l	0.88l	1.75l	1.75l
Specific energy	206Wh/ kg	427Wh/ kg	205Wh/ kg	398Wh/ kg
Energy density	239Wh/ l	565Wh/ l	256Wh/ l	491Wh/ l

4:15 - 4:45 Overview of the Development and Use of Nanostructured Metal Oxides in Rechargeable Li Batteries - J. Adams, I. Exnar & M. Graetzel, Xoliox S.A, Switzerland

4:45 - 5:15 Lithium Metal Phosphates - Next Generation Materials
M.Y. Saidi, H. Huang, J. Swoyer & J. Barker, Valence Technology

5:15 - 5:45 Electronically Conductive Phospho-olivines as Lithium Storage Electrodes - Y-M Chiang, S-Y Chung, J. Bloking & A. Andersson, MIT and A. Gozdz, A123 Systems and P. Limthongkul, National Metal and Materials Technology Center, Thailand

5:45 - 6:15 The Mechanisms of Capacity Loss in Li Ion Batteries - R. Yazami, Cal. Inst. Tech.

6:00 - 7:00 **EXHIBIT AREA OPEN / COCKTAILS**

Wednesday, March 19

Small Fuel Cells

8:30 - 9:00 Small Fuel Cells vs. Li Ion Battery: A Battery Manufacturer's View - K. Kelty, Panasonic

9:00 - 9:30 The Case for Fuel Cell/Battery Hybrids - F. Gibbard, Gibbard R&D Corp.

9:30 -10:00 An Ultra Compact High Power Density Fuel Cell for Portable Electronics - J. Morse, LLNL

10:00 -10:15 Break

10:15 -10:45 Small Fuel Cells for Portable Power Applications - S. Gottesfeld, MTI

10:45 -11:15 Hydrogen Fuel Cell Systems for Consumer Electronics - A. Briggs, Millennium Cell

11:15 -11:45 Recent Advances in Battery Management - D. Freeman, Texas Instruments

11:45 -12:15 Progress in Advanced Batteries for Portable Consumer Devices - P. Cheeseman, Rayovac

12:15 - 2:00 **Lunch served in the EXHIBIT area**

HEV/42V Batteries

2:00 - 2:30 Development of Li Ion Battery for EV and E-Bicycle - R. Wang, BYD

2:30 - 3:00 Advanced NiMH Battery Technology - M. Fetcenko, S. Ovshinsky & S. Dhar, Ovonic Battery

3:00 - 3:30 Freedom Car/USABC Current Status - H. Tataria, General Motors

3:30 - 4:00 Recent Developments for HEV Batteries - J. Carcone, Sanyo

4:00 - 4:15 Break

15 - 4:45 NiMH and Li Ion Batteries for HEV Applications: Performance, Limitations and Recommendations for Improvement - J. McBreen, Brookhaven National Laboratory

4:45 - 5:15 Advanced Li Ion Batteries for Automotive Applications - F.J. Kruger & M. Schweizer-Berberich, GAIA, Germany and A. Manning & R. Turi, Lithium Technology Corp.

5:15 - 5:45 Application of Battery Management Technology for Enhanced Reliability & Performance in 42V and HEV Systems - L. Hruska, Microchip Technology

5:45 - 6:15 Thin Layer Li Batteries: Electrode and Electrolyte Materials, Production and Testing Methods E. Shembel, Y. Kalynushkin, V. Redko, P. Novak & T. Pastushkin, ENER1

6:00 - 7:00 **EXHIBIT AREA OPEN / COCKTAILS**

Thursday, March 20

Battery Safety and Performance

7:45 - 8:15 Coffee and Pastry

8:15 - 8:45 Enhancements to the Cycle Life of Consumer RAM Batteries
J. Daniel-Ivad, K. Kordesch, E. Daniel-Ivad & L. Duong, BTI

8:45 - 9:15 Thermal Modeling and Management of Li-ion Battery Products
H. Maleki and J. Howard, Motorola

9:15 - 9:45 Predicting Li Ion Battery Safety Quickly and Accurately - C. Lampe-Onnerud, TIAX

9:45 -10:15 Advances in Polymer PTC Battery Products - J. Kelly & G. Straker, Bourns

10:15 -10:30 Break

10:30 -11:00 Efficient Incorporation or PPTC Devices in Pack Designs for Tomorrow's Portable Electronics
M. Galla, Tyco Electronics

11:00 -11:30 Novel Halide-free Conducting Salts for Lithium Batteries - U. Wietelmann, Chemetall GmbH

11:30 -12:00 ~~Performance Tests for 10AH Land Warrior Prototype Li Ion Polymer Battery~~
~~G. Au, L. Cristo, A. DeAnni & J. Rafferty, U.S. Army~~

12:00 -12:30 Development of 25 Ah and 50 Ah Lithium/Polycarbon Monofluoride Envelope Cells
C. Giwa, A. Ritchie, E. Eweka, P. Bowles & A. Gilmour, QinetiQ and A. Gilmour, Lexell Technology

QINETIQ

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SEMINAR PROGRAM

Monday, March 17, 2003

8:30 -10:15 **Pre-Seminar Tutorial I** - New Advances in Materials for Li Ion Batteries and Competition from Microfuel Cells - J. Dahn, Dalhousie University

10:30 -12:15 **Pre-Seminar Tutorial II** - Worldwide Market Update on NiMH, Li Ion and Polymer Batteries for Portable Applications and HEVS - H. Takeshita, IIT, Japan

OEM Perspectives / Battery Developments
Moderators - N. Allen, Power Strategies and H. Taylor, Consultant

1:00 - 1:30 A Twenty Year Perspective of Portable Energy Systems and Future Prospects
K. Brandt, Ionity

1:30 - 2:00 A Global Perspective of Alternative Energy Vehicle Technology
R. Stempel, Chairman, Energy Conversion Devices, Inc.

2:00 - 2:30 HEV and 42V PowerNet: Drivers and Trends - N. Allen, Power Strategies

2:30 - 3:00 Cell Phone User Profiles and Direction for New Devices - S. Engstrom, Motorola

3:00 - 3:30 Trends in Mobile Computing & Proposed Standards - J. Layton, Dell

3:30 - 3:45 Break

3:45 - 4:15 Mobile PC Extended Battery Life Working Group: An Overview - K. Shah, Intel

4:15 - 4:45 Trends in Notebook Computing, Enhanced Mobility and Resultant Energy Implications
T. Hildner, IBM

4:45 - 5:15 Industry and Consumer: Perception and Reality - S. Bard, Symbol Technologies

5:15 - 5:45 Advanced Primary Batteries for New and Emerging Devices - M. Roberts, Duracell

5:45 - 6:15 New Product Concepts from Energizer - J. Grady, Energizer

6:15 - 6:30 Introduction to Chinese Battery Delegation: A Technical and Business Perspective of the Chinese Battery Industry

6:30 - 8:00 **COCKTAIL RECEPTION -- OPENING OF EXHIBIT AREA**

Tuesday, March 18

Li Ion Batteries

8:15 - 8:45 New Progress on R&D and Production of Li Ion Batteries in China
J. Wang , Tianjin Institute of Power Sources

8:45 - 9:15 SKC Li Ion Polymer Batteries - Z. Zhang, C. Park, C. Chai, SKC America

9:15 - 9:45 R & D of Li Ion Prismatic Cells
G. Li, Y. Pan & D. Wang, Shanghai Institute of Space Power Sources

9:45 -10:15 Philips Curved-Lithylene Battery for Greater Design Freedom of Portable Products
H. Feil, Philips

10:15 -10:30 **Break Sponsored by ABT *(Advanced Battery Technology)***

10:30 -11:00 Large Format Li Ion Batteries Using Novel Electrode Materials - B. Ammundsen, Pacific Lithium

Battery Materials -- Moderator - Y. Nishi, President, Sony Materials Co.

11:00 -11:30 Synthesis and Electrochemical Performance of Li Mn O Systems - J.S. Xue, B&K Technology Co. Ltd., China and X. Li, M. Xu & X. Wu, Central South University, China

11:30 -12:00 Advances in Carbonaceous materials for Primary and Secondary Batteries
I. Barsukov, Superior Graphite

12:00 -12:30 The Role of Morphology on Battery Active Electrode Material Performance
L. Dominey, L.A. Dominey Assoc.

12:30 - 2:00 **Lunch served in the EXHIBIT area**

2:00 - 2:30 Limitations of Electrode Materials for Li Batteries: Where to From Here - M. Thackeray, ANL

2:30 - 3:00 Alloy Anodes for Li Ion Batteries - J. Dahn, Dalhousie Univ.

3:00 - 3:30 Plasma Sprayed Electrodes for Thermal and Rechargeable Li Batteries and Intermediate Temperature SOFCs - D. Reisner, J. Dai, R. Hui, J. Roth & J. Broadhead, US Nanocorp and F. Reinhardt & R. Guidotti, Sandia National Laboratories

3:30 - 4:00 Nano Materials with Respect to the Field of Energy Storage: Science vs Applications
J-M Tarascon, S. Grugeon, S. Laaruelle, D. Larcher, G. Amatucci & L. Dupont, Univ. de Picardie Jules Verne, France

4:00 - 4:15 Break